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Vibrational spectra from data of subsystems

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Although NMR spectroscopy and X-ray analysis are the most widely used analytical tools in a synthetically oriented lab, vibrational spectroscopy is still of importance. An advantage of IR spectroscopy, especially when compared to NMR spectroscopy, is that it has a much higher sensitivity and that it can be performed faster. A major disadvantage, however, is that there is no direct way from the spectrum to structural features of the system studied. Therefore the well established method of structure elucidation by means of vibrational spectroscopic data is the comparison of calculated and experimental spectra. Using this approach in combination with NMR spectroscopic data one can often do calculations on smaller systems, e.g. systems which have a substituent as t-butyl replaced by methyl (or even hydrogen). This, of course, does not work in the case of vibrational spectroscopy. One always has to perform a calculation on the 'full' system including all substituents and groups. Despite the successes in computer technology as well as in the area of code development which lead to higher and higher performance of the programs used there are always molecules which are to large to perform calculations of a sufficient accuracy on.

Within the approach we present here the hessian of the target molecule is built up from the hessians of smaller systems, e.g. parent compound + models of substituents, (overlapping) parts of the target moelcule. The built up process is done using the so-called 'primitive internals', i.e. a full set of valence coordinates, stretches, bends and torsions /1/. Internal coordinates, especially redundant internal coordinates, have recently been used successfully not only in geometry optimizations but also to scale the calculated force constants /1/.

The built up process will work well only if the force constants are transferable from the source molecules to the target and if the couplings between the parts of the target system represented by different source molecules are negligible.

We discuss some illustrative examples, e.g. substituted diphosphenes, heterocubanes, porphines and aromatic compounds. They fulfill the requirements mentioned to a different degree.

/1/ J. Baker, A. A. Jarzecki, P. Pulay J. Phys. Chem. A, *1998* **102** 1412